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PROVISIONAL SPECIFICATION

Applicant(s):

MEGGITT (UK) LTD

Invention Title:

STEAM REFORMER

The invention is described in the following statement:

## STEAM REFORMER

### INTRODUCTION

Heatric has been involved in the commercial design and manufacture of "micro/milli" scale heat exchange core matrices called Printed Circuit Heat Exchangers (PCHEs) since 1985, following several years of developmental work at the University of Sydney. PCHEs are single-material (usually metal) matrices formed by diffusion bonding together plates into which fluid flow passages have (usually) been formed by photo-chemical machining. Complex fluid circuitry is readily implemented with this technique, and minimum passage dimensions are generally dictated by the cleanliness of the fluids and allowable pressure drops.

With headers and nozzles attached to the PCHE cores, the complete heat exchangers are highly compact, typically comprising about one-fifth the size and weight of conventional shell-and-tube exchangers for the same thermal duty. PCHEs are "compact" relative to conventional heat exchangers, but they are not necessarily "small". Single units of up to 100 tonnes have been manufactured, and clearly these are only "compact" in comparison to the 500 tonne alternatives.

Currently there are thousands of tons of such matrix in hundreds of services - many of them arduous duties on offshore oil and gas platforms where the size and weight advantages of compact structures are of obvious major benefit. Whilst these matrices are predominantly involved in thermally simple two-fluid heat exchange, albeit at pressures up to 500 bar, there also is a long history of their application to more complex integrated fluid processing applications. Indeed even in the development stage of PCHE technology at the University of Sydney operations such as multi-stream counterflow heat exchange, rectification, stripping, mixing, absorption, boiling, condensation and separation were incorporated into compact integrated process modules. The potential for application of PCHEs to temperature control in chemical reaction has also been long recognised, with potential benefits anticipated in areas such as compactness, operability, efficiency, safety and cost.

The process integration principles presented here are applicable to both large- and small-scale syngas generation, but are illustrated with reference to a small-scale steam methane reforming process for a stationary Proton Exchange Membrane Fuel Cell (PEMFC). A small-scale methane reformer would also have potential application in distributed hydrogen/syngas production for other purposes, using the natural gas pipe network for the supply or processing stranded natural gas.

### TEMPERATURE CONTROL IN REACTORS

**Tubular reactors** The temperature in static catalyst beds with high heat load, such as reformers, is conventionally controlled by packing the catalyst into tubes, with heat transfer from the outside of the tubes maintaining the radial and axial temperature profiles inside the tubes within acceptable bounds. This has been a very successful strategy, but does require the striking of a delicate balance between reaction and heat transfer within the tubes, heat transfer to the outside of the tubes, and pressure drop.

One outcome of this balance is that tubular reformers are bulky since relatively large catalyst particles with low effectiveness are employed. Xu and Froment<sup>1,2</sup> calculate an effectiveness of the active catalyst of less than 3%

for the reforming reactions, with the active catalyst applied to only the outer 2 mm of the catalyst particles they considered. The implication is that the reforming catalyst bed could be two-orders of magnitude smaller if effectiveness could be held near to 1 simply by the use of small catalyst particles, without any improvement of intrinsic activity. Xu and Froment examined the intrinsic kinetics using particles 0.18-0.25 mm. Small particles are incompatible with tubular reformers, however, because pressure drop constraints would dictate the use of many parallel, short tubes.

**Catalytic plate reactors** The possibility of applying a thin layer of reforming catalyst on to the surfaces of micro-reactors has been much discussed in recent years, with Ramshaw<sup>3</sup> an early proponent, and there is no doubt that PCHE cores would constitute an excellent matrix for such an approach. However whilst this technique has great promise in appropriate circumstances, certain difficulties remain, including:

- Adhesion of the catalyst to the metal substrate
- Difficulties with catalyst life and replacement
- Coupling of the heat transfer and catalyst areas - generally requiring very high activity catalyst if over-investment in heat exchange surface is to be avoided.

**Multiple adiabatic beds** An alternative approach illustrated in this presentation is the use of multiple adiabatic beds, with heat interchangers between the beds. This is of course quite a traditional approach to temperature control in chemical reaction, but combined with PCHEs certain advantages arise:

- The flexibility of PCHEs allows them to be configured cost-effectively as panels between the beds, avoiding interconnecting piping and the need to redistribute the reactants to each bed after heat exchange. Thus many stages of adiabatic reaction and heat exchange can be employed, making the approach applicable to high heat load reactions such as reforming. A saw-tooth temperature pattern will result, with the size of the teeth inversely proportional to the number of them, so that temperatures can be held between any required bounds. Overall isothermal, ascending or descending temperature profiles can be applied to the reaction.
- The catalyst beds can be presented to the reactants with a short flow path and large face area, allowing the use of small catalyst particles with high effectiveness. Very much more compact reactors can result from this, as noted above.
- Conventional, proven catalyst forms can be employed in configurations which allow ready replacement of the catalyst in accessible, "large" slots. The only variation which might be preferred for the catalyst is smaller particle sizes than for tubular reactors to assist process intensification. Crushing of conventional sizes is a makeshift option. In many cases a preferred catalyst form would be coated ceramic monolith, in order to minimise pressure drop.
- The heat transfer volume and catalyst volume in the reactor are decoupled. Depending on the heat loads and heat transfer fluid temperature, the ratio between the two volumes can be varied at will.
- Flow patterns within the PCHE panels can be configured to produce flat temperature profiles in the reactants, avoiding hot-spots.
- Periodic injection of fresh reactants is readily incorporated, thereby allowing the extent of exothermic reactions to be safely limited in each stage.

In a reformer two reactions are occurring: the reforming reaction itself, and also the combustion reaction supplying the heat to the reformer. Both are subject to the multiple adiabatic bed approach.

## HEAT RECOVERY

When the reaction occurs at high or cryogenic temperatures, the feed-effluent exchangers for the reactor are critical to overall process efficiency. PCHEs are well suited to high-temperature, high-pressure, high-effectiveness counterflow heat exchange duties, with multi-stream contact an option. Counterflow exchangers with over 40 NTUs have been subject to successful performance verification.

In addition to recovering heat, the feed/effluent trains for the reforming process also need to deliver the process fluids to further reactors - pre-reformers, water gas shift (WGS), selective CO oxidation - at appropriate temperatures, preferably with minimal or no control. Appropriate process configurations and contacting arrangements within the PCHEs can assist with this.

## STEAM REFORMER DESIGN BASIS

The general points discussed above are illustrated below with reference to a PEMFC steam methane reformer, whose design basis is taken to be:

- 4 bara process side pressure, atmospheric combustion side pressure
- CO-free (<10 ppm) hydrogen required
- Stand-alone system - no scope for export or import of steam. Heat rejection temperature from fuel cell too

- low for steam raising
- Simple, robust control required - no more complex than an industrial refrigeration system
- High efficiency
- Anode off-gas used for combustion heat
- Conservative design with respect to carbon formation
- Compact and robust, for ease of transport and installation
- Suited to low-cost manufacture
- Sulphur-free methane feed

## PROCESS CONFIGURATION

Many process configurations are of course possible, depending on the relative constraints on efficiency, cost, size, operability and so on. For illustrative purposes the process of Figure 1 is discussed. Whilst the network of 20 heat exchangers and 27 catalyst beds appears relatively complex for a small system, it is in fact readily implemented with PCHE technology, as complex fluid circuits do not necessarily add to manufacturing complexity.

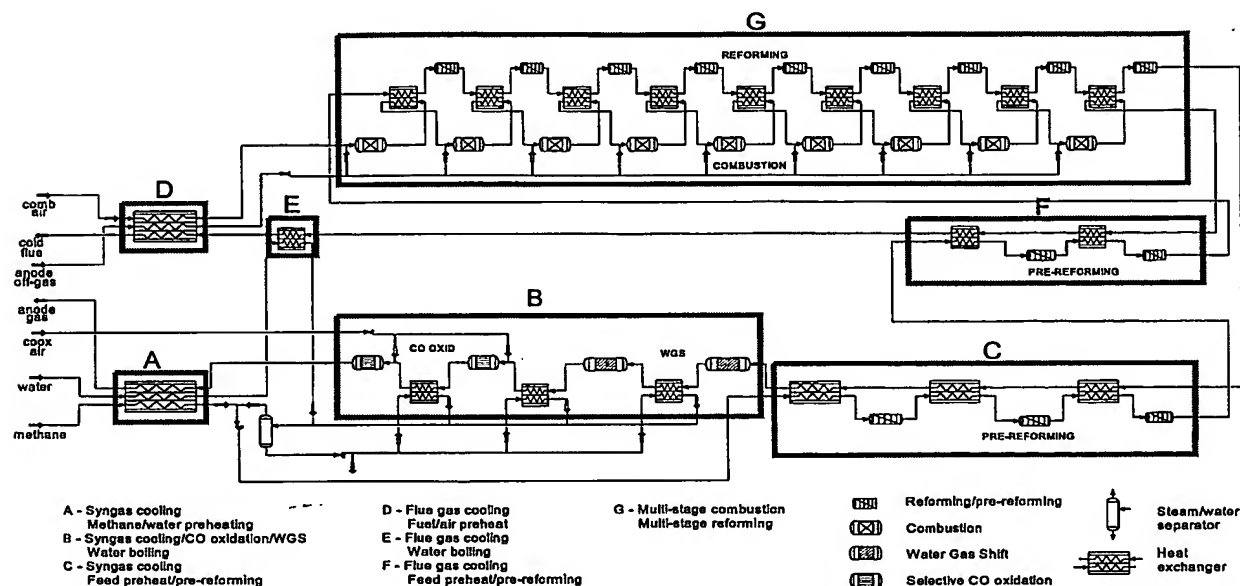


Figure 1: Steam methane reformer PFD for 4 bara PEMFC, SR = 2.6

**Ascending reforming temperature profile** The feed gas is subject to stagewise reforming, consisting of:

- 3 pre-reformers heated by hot syngas
- 2 pre-reformers heated by hot flue gas
- 9 reformers indirectly heated by catalytic combustion of anode off-gas.

The reforming temperature profile is shown in Figure 2.

The maximum reforming temperature remains below 800°C because higher temperatures are not essential at these low pressures: a small amount of methane slip simply constitutes an inert at the fuel cell anode and is ultimately burnt usefully in the combustors.

In the relatively low temperature pre-reforming stages higher hydrocarbons are converted and the hydrogen content is increased well below methane cracking temperatures. According to Ridler & Twigg<sup>4</sup>, above 650°C carbon formation from methane cracking becomes faster than the carbon removal reactions if the methane cracking equilibrium is unfavourable, hence high hydrogen levels are required by the time

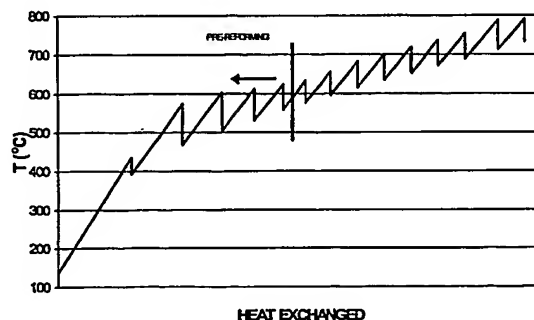


Figure 2: Reforming temperature profile

this temperature is reached. The six stages of reforming and pre-reforming below 650°C are helpful in ensuring carbon activity remains below 1 above 650°C. Assuming no reaction occurs in the heat exchangers between reforming stages, each temperature spike represents a departure from reforming equilibrium conditions towards cracking conditions. At lower steam ratios (SRs) than the 2.6 employed in this study, more than 9 reforming stages might be preferred to retain a clear safety margin over methane cracking.

**Efficiency** The limiting efficiency for the 4 bara steam reforming process using anode off-gas as the combustion heat source and the stoichiometric SR of 2 is 89.2% (based on Lower Heating Value (LHV)). This is slightly lower than the efficiency achievable with methane combustion driving the reforming process but combustion of the anode off-gas avoids gross inefficiency arising in the fuel cell from concentration polarization at the anode.

The boiling of water for steam represents a substantial unrecoverable heat load in the process. Increasing the SR from 2 to 3 results in a 6% loss in achievable efficiency, but low SR results in increased methane slip and tends to favour methane cracking. An intermediate SR of 2.6 arises from the heat recovery configuration of Figure 1. Alternative schemes could result in different SRs: for example, higher SRs would arise with less flue gas preheating of the process stream in F, and lower SRs would arise if more flue gas heat were applied to preheating the combustion air rather than boiling water in E.

The other major loss of reforming efficiency arises from the discharge of hot effluent streams. As shown in Figure 3, the temperature pinch between the composite feed and effluent streams occurs at the cold end (below the water boiling point). Figure 4 shows the approximate dependency of efficiency (both on a LHV basis and as a percentage of the maximum achievable) on the cold pinch.

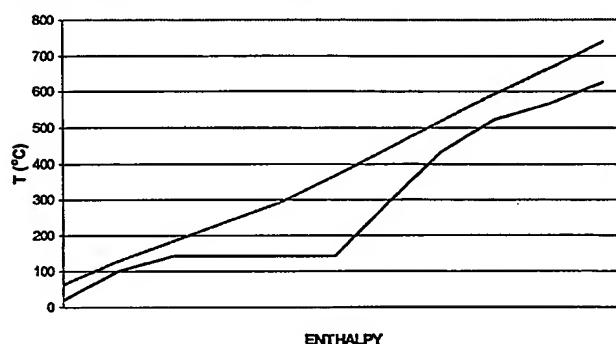


Figure 3: Composite feed and effluent curves for reformer

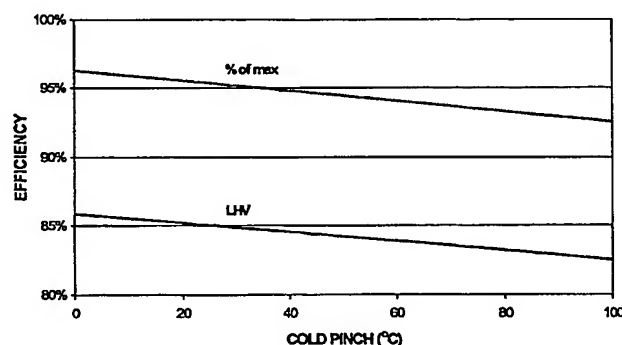


Figure 4: Efficiency versus cold pinch, SR = 2.6

Ignoring heat losses, the efficiency for the process of Figure 1 is 85.2% (LHV), which is approximately 95.5% of the maximum, comparing favourably with efficiency levels achieved industrially at very large scale.<sup>5</sup>

**Control** Numerous control elements are clearly not desirable in small-scale, distributed systems, and the layout of Figure 1 incorporates substantial elements of passive (self-regulating) control:

- Heat exchangers are sized and configured such that the temperature profile shown in Figure 2 is maintained even under conditions of substantial turn-down. Only the maximum reformer temperature requires independent control through the fuel supply rate.
- Counterflow and co-flow exchangers are employed. Both pinch up as flow rates fall, without substantially affecting boundary temperatures.
- The parallel splits in the fuel supply to the catalytic combustors, the air supply to the two (or more) stages of selective CO oxidation, and water to the boilers are "hard-wired" into the assemblies, and require no active control.
- Water is supplied at the rate required to maintain level in the phase separator, from which there is a net outflow of process steam and a small liquid blow-down. The steam ratio remains reasonably constant with capacity as the availability of heat to raise steam varies with the methane throughput.

## CONCLUSIONS

PCHE technology supports the cost-effective manufacture of complex process modules in highly compact assemblies and is applicable to both large- and small-scale steam reforming systems. Efficient and flexible heat exchangers support not only high levels of thermal efficiency, but can also assist in the simplification of control. The process modules are readily adaptable to allow the use any catalyst - whether traditional forms and sizes or high-activity variants - with straightforward changeout of spent catalyst.

## APPENDIX - DETAILED DISCUSSION OF FIGURE 1 PROCESS

**Feed/Effluent Trains ABC and DEF** Whilst it would be possible in principle to incorporate all the feed and effluent streams into multi-stream exchangers, for the most part two-stream exchangers are adequate. Figures 5 and 6 chart the temperature profiles for the syngas and flue gas heat recovery respectively, showing that a reasonable balance between hot and cold stream heat capacities can be struck without the universal use of multi-stream exchangers. The large heat requirement for steam raising is obvious from the horizontal portions of the charts, and a small amount of water condensation is evident in the syngas in Figure 5.

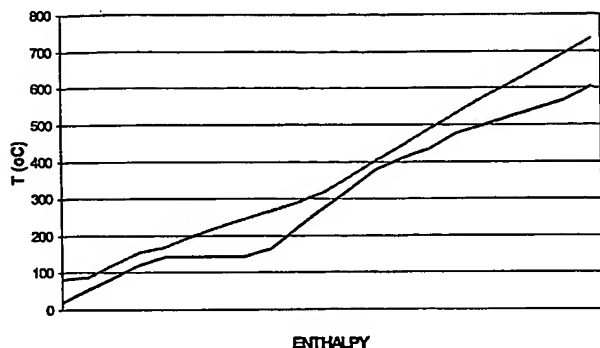


Figure 5: Heat recovery from hot syngas

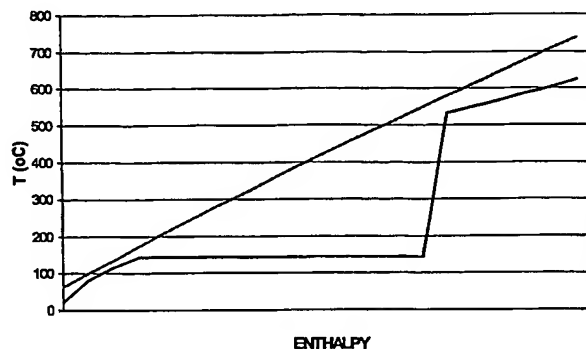


Figure 6: Heat recovery from hot flue gas

**A - Syngas Cooling; Water and Methane Preheating** A three-stream heat exchanger is employed to preheat the water (below the boiling point) and methane in the final cooling step for the syngas. An internal pinch occurs at the point where water condensation begins on the syngas side. The three-stream counterflow exchanger:

- Permits relatively high effectiveness to be achieved, as shown in Figure 5.
- Avoids a controlled split of the syngas stream to preheat the methane and water streams in separate exchangers.

**B - Syngas Cooling/CO selective oxidation/Water Gas Shift; Water Boiling** Carbon monoxide levels must typically fall below 10 ppm for a PEMFC. Currently this requires a selective oxidation (COOX) reaction following the WGS, as carbon dioxide removal is not practical in a small system and no suitable selective methanation catalyst appears to be available (with methanation of the CO<sub>2</sub> continuing after exhaustion of the CO). Both reactions are shown as occurring in two stages in this configuration. The COOX reaction introduces a small amount of nitrogen to the syngas, and consumes a small amount of the hydrogen.

The heat load for steam raising is relatively high - about two-thirds of that required from combustion in the reformer. Much of the heat recovery from the hot process streams is therefore committed to water boiling. Both the exothermic WGS and COOX reactions can run above the water boiling point, contributing to the steam raising.

Water is shown as boiling in a thermosyphon loop in the heat exchangers following these reactions as this:

- Provides an opportunity for blow-down, minimising the quality requirements on make-up water, and
- Avoids dryout on the heat exchange surfaces at high vapour quality.

**C - Syngas Cooling; Feed Preheat/Pre-Reforming** Above the water boiling point, the heat from the hot syngas preheats the feed stream. Sufficient heat is available to drive three stages of preheat, which is favourable for several reasons:

- C<sub>2</sub>+ molecules in the feed are converted to methane at low temperatures, without risk of coking
- Hydrogen levels are increased at low temperature, without risk of methane cracking
- High-grade heat is used for high-grade purposes (reforming)
- If the first pre-reforming catalyst were sufficiently sulphur resistant, hydrogen for a following HDS unit could be generated without hydrogen recycle.

The two left exchangers in this series are counterflow exchangers and the third is co-flow, in order to lock in the required temperature profile during turndown. Without co-flow in the third exchanger there would be a danger of overheating the feed stream and thereby cracking methane.

**D - Flue Gas Cooling; Fuel/Air Preheat** Once again a three stream exchanger is employed, with the fuel and air preheated separately without the need for a controlled split of the flue. The air passes sequentially through all the stages of catalytic combustion, whilst the fuel must be metered to the combustors in parallel in order to limit the temperature rise in each stage, and hence premature mixing must be avoided. Despite being cooled to quite low temperatures, there is no water condensation from the flue gas.

**E - Flue Gas Cooling; Water Boiling** In the scheme shown in Figure 1, most of the steam is raised in this exchanger. The exchanger operates as a once-through boiler as the exit quality remains below 70%, avoiding the threat of dry-out. The amount of heat available from the flue gas for steam raising in this exchanger depends on how much is consumed elsewhere. In alternative configurations, more heat would be available for steam raising if heat exchange with the syngas stream were eliminated in module F. Less heat would be available for steam raising if a split of the flue gas stream were to be used to further preheat the combustion air and fuel in D.

**F - Flue Gas Cooling; Feed Pre-Heat/Pre-Reforming** Two additional stages of pre-reforming generate more relatively low temperature hydrogen, further protecting the reformer itself from methane cracking. The left exchanger is counterflow and the right exchanger is co-flow, once again in order to lock in the required temperature profile during turndown, without risk of overheating the feed.

**G - Stagewise reforming and combustion** The reformer consists of nine stages of reforming reaction driven by nine stages of anode off-gas combustion. The reactions on both sides occur in essentially adiabatic beds, with heat exchange occurring between the fluids as they pass between the adiabatic beds. More or fewer than nine stages could be employed, and whilst the arrangement of Figure 1 is convenient in certain respects it is not in fact essential that the number of combustion and reforming stages should be identical or nearly identical.

A larger number of reforming stages would reduce the departure from equilibrium with each re-heat of the syngas, though 9 stages does permit a conservative margin over methane cracking for SR of 2.6.

Within the reformer module, special fluid circuitry provides for:

- The splitting of the anode off-gas into 9 parallel streams, and
- The further subdivision of the fuel in those streams into numerous parallel streams for intimate mixing into the combustion air prior to combustion at each stage.

The ascending temperature profile shown in Figure 2 for the reformer is driven by this circuitry without further active control. Only the maximum reformer temperature requires continuous control through the total fuel supply rate.

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**RELATED APPLICATIONS**

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HEATRIC PTY LTD

By their Patent Attorneys

GRIFFITH HACK

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